

Thermodynamics of Carbonates and Hydrates Related to Heterogeneous Reactions Involving Mineral Aerosol

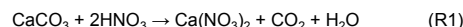
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Background

Mineral aerosol may alter photochemical oxidation cycles by serving as a reactive surface in the troposphere. Calcium carbonate is thought to be a particularly reactive component of mineral aerosol. An overall reaction of the form



has been proposed as a sink for tropospheric nitric acid.

Laboratory investigations of R1 indicate that nitric acid is irreversibly acquired by CaCO_3 to form $\text{Ca}(\text{NO}_3)_2$, CO_2 , and H_2O . Results of these experiments have been used to suggest that R1 irreversibly removes HNO_3 from the gas phase in the atmosphere. However, the CaCO_3 in the experiments was exposed to HNO_3 in an inert carrier gas, whereas the atmosphere contains a significant background concentration of CO_2 , which would tend to drive R1 in reverse.

Related to the question of the reversibility of R1 under atmospheric conditions is the uncertainty regarding the state of the $\text{Ca}(\text{NO}_3)_2$ product in R1. Specifically, the crystalline form of $\text{Ca}(\text{NO}_3)_2$ for low-RH conditions is unclear. The thermodynamically stable crystalline form of $\text{Ca}(\text{NO}_3)_2$ in the bulk for typical atmospheric conditions (e.g., $T = 298 \text{ K}$, $\text{RH} = 45\%$) is a tetrahydrate, yet metastable states may exist in the atmosphere. The crystalline form of $\text{Ca}(\text{NO}_3)_2$ is significant because it influences the equilibrium disposition of reactions involving CaCO_3 and HNO_3 . Assuming for the moment that $\text{Ca}(\text{NO}_3)_2$ exists in the atmosphere as a stable hydrate, a question arises on how to determine its deliquescence relative humidity (DRH), since no expression for the variation of DRH with temperature has been reported for hydrated salts.

We use an equilibrium thermodynamics approach to address some of the questions just raised. We consider a more general form of R1:



where $\text{X} = \text{Ca}$ or Mg , $\text{Y} = \text{NO}_3$ or Cl , and n is the hydration number of the XY_2 salt.

Objectives

The goals of this study are as follows:

- To determine the thermodynamically preferred state governed by R2 under atmospheric conditions.
- To derive an expression for the variation of the DRH for hydrated salts with temperature and to assess the significance of differences in DRH(T) for anhydrous and hydrated forms of the XY_2 salts.

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Approach

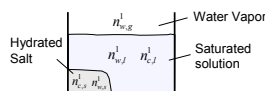
Reversibility of R2: We investigate the equilibrium disposition of R2 by determining equilibrium concentrations of HY (i.e., HNO_3 and HCl) under atmospheric conditions. For $[\text{HY}]_{\text{ambient}} > [\text{HY}]_{\text{equilibrium}}$, the forward direction of R2 is thermodynamically preferred; for $[\text{HY}]_{\text{ambient}} < [\text{HY}]_{\text{equilibrium}}$, the reverse direction is thermodynamically preferred.

DRH(T) for hydrates: Wexler and Seinfeld (1991) derive the following for DRH(T) for anhydrous salts:

$$\text{Anhydrous Salt: } \frac{d \ln \text{DRH}}{dT} = \frac{n_{\text{sat}} L_s}{RT^2} \quad (1)$$

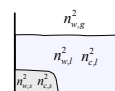
L_s = Latent heat of fusion of salt
 R = gas constant; T = temperature
 n_{sat} = moles of solute per mole of water in saturated solution at DRH

- (1) is for an **anhydrous-salt system** at DRH (i.e., a saturated electrolyte solution in equilibrium with water vapor and the *anhydrous* crystalline salt). n_{sat} occurs in (1) because n_{sat} moles of solute precipitate from the saturated solution to maintain equilibrium when 1 mole of water evaporates.
- For a **hydrated-salt system** at DRH (where equilibrium involves the *hydrated* crystalline salt), the number of moles of salt that crystallize to maintain equilibrium when 1 mole of water evaporates is determined here by considering mass conservation for states before and after evaporation.



State 1: Hydrate system in equilibrium before evaporation of 1 mole of H_2O .

n = # of moles; s = solid
 c = salt; l = liquid
 w = water; g = gas



State 2: Hydrate system in equilibrium after evaporation of 1 mole of H_2O .

$$\text{H}_2\text{O mass balance: } n_{w,g}^1 + n_{w,l}^1 + n_{w,s}^1 = n_{w,g}^2 + n_{w,l}^2 + n_{w,s}^2 \quad (2)$$

$$\text{Crystal mass balance: } n_{c,l}^1 + n_{c,s}^1 = n_{c,l}^2 + n_{c,s}^2 \quad (3)$$

$$n_{w,g}^2 = n_{w,g}^1 + 1; \quad n_{sat} = n_{c,l}^1 / n_{w,l}^1; \quad n = n_{w,s}^1 / n_{c,s}^1 \quad (4)$$

$$\text{From (2) - (4): } n_{c,s}^2 - n_{c,s}^1 = \frac{n_{sat}}{1 - n \cdot n_{sat}}$$

$$\text{Hydrated Salt: } \frac{d \ln \text{DRH}}{dT} = \frac{n_{sat}}{1 - n \cdot n_{sat}} \frac{L_s}{RT^2}$$

$$\ln \frac{\text{DRH}(T)}{\text{DRH}(T_o)} = \frac{n_{sat}}{1 - n \cdot n_{sat}} \frac{L_s}{R} \left(\frac{1}{T_o} - \frac{1}{T} \right) \quad (5)$$

Variation of DRH with Temperature

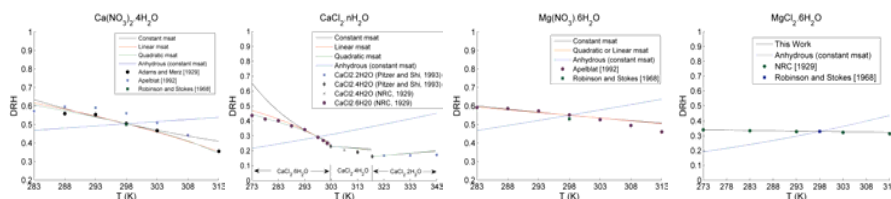


Fig. 1. Comparison of measurements with predictions of (5) and similar expressions that account for the temperature dependence of n_{sat} .

Equilibrium Concentrations

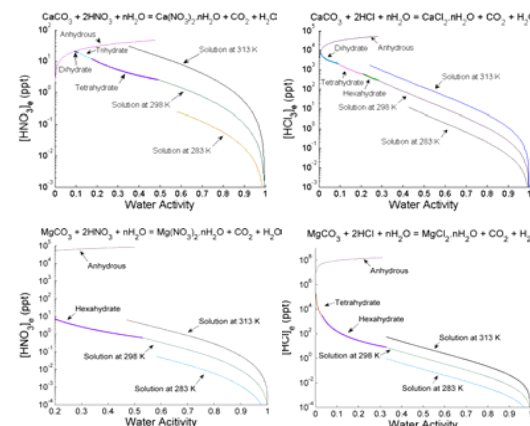


Fig. 2. Equilibrium concentrations of HNO_3 and HCl . The form of R2 and the stable-hydrated form of the $\text{XY}_2 \cdot \text{nH}_2\text{O}$ salt are indicated in the figure.

Conclusions

- A new expression (5) adequately predicts DRH(T) for hydrated salts (Fig. 1). DRH(T) is markedly different for anhydrous and hydrated salts (Fig. 1).
- The forward direction of R2 is thermodynamically preferred for reactions containing $\text{XY}_2 \cdot \text{nH}_2\text{O}$ in the stable-hydrated form for typical low-RH conditions. These reactions scavenge HNO_3 and HCl from the gas phase.
- The forward direction of R2 is sometimes prohibited for reactions containing anhydrous XY_2 for low-RH situations common in the troposphere. Behavior in this situation is dependent on solid-phase nucleation kinetics.
- The reverse direction of the R2 reaction containing aqueous CaCl_2 solution is thermodynamically preferred under some dry tropospheric conditions. This reaction releases HCl into the gas phase.
- One should consider hydrated salts when modeling reactions of the form of R2 in low RH situations.

The research described in this poster is discussed in more detail in Kelly and Wexler (2005) JGR [in press]